

## PATENT COOPERATION TREATY

PCT

From the INTERNATIONAL BUREAU

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)Date of mailing (day/month/year)  
25 April 2001 (25.04.01)To:  
WOLFF, BREGMAN AND GOLLER  
P.O. Box 1352  
91013 Jerusalem  
ISRAËLApplicant's or agent's file reference  
131,652 PCT

## IMPORTANT NOTIFICATION

International application No.  
PCT/IL00/00513International filing date (day/month/year)  
29 August 2000 (29.08.00)

## 1. The following indications appeared on record concerning:

 the applicant     the inventor     the agent     the common representative

Name and Address  SATEC ECOCHEM LTD. Har Hachotzvim Science Based Industrial Park P.O. Box 45022 91450 Jerusalem Israel	State of Nationality IL	State of Residence IL
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	Facsimile No.	
	Teleprinter No.	

## 2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

 the person     the name     the address     the nationality     the residence

Name and Address  JOMA CHEMICAL AS 7898 Limingen Norway	State of Nationality NO	State of Residence NO
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

## 3. Further observations, if necessary:

Please forward powers of attorney to the International Bureau.

## 4. A copy of this notification has been sent to:

<input checked="" type="checkbox"/> the receiving Office	<input checked="" type="checkbox"/> the designated Offices concerned
<input type="checkbox"/> the International Searching Authority	<input type="checkbox"/> the elected Offices concerned
<input type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland  Facsimile No.: (41-22) 740.14.35	Authorized officer  Jean-Marie McAdams  Telephone No.: (41-22) 338.83.38
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## PATENT COOPERATION TREATY

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>131,652 PCT</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/IL 00/00513</b>	International filing date (day/month/year) <b>29/08/2000</b>	(Earliest) Priority Date (day/month/year) <b>30/08/1999</b>
Applicant <b>SATEC ECOCHEM LTD. et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 4 sheets.

It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

contained in the international application in written form.

filed together with the international application in computer readable form.

furnished subsequently to this Authority in written form.

furnished subsequently to this Authority in computer readable form.

the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2.  **Certain claims were found unsearchable** (See Box I).

3.  **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

the text is approved as submitted by the applicant.

the text has been established by this Authority to read as follows:

SULFATISATION PROCESS FOR METAL EXTRACTION FROM SULFIDE ORES

5. With regard to the **abstract**,

the text is approved as submitted by the applicant.

the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

as suggested by the applicant.

because the applicant failed to suggest a figure.

because this figure better characterizes the invention.

1

None of the figures.

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/IL 00/00513

## Box III TEXT OF THE ABSTRACT (Continuation of item 5 of the first sheet)

The invention provides a hydrometallurgical process for treating metal-containing sulfide ores and concentrates, comprising reacting said metal-containing sulfide with concentrated sulfuric acid at a temperature of between about 300°C and 400°C in the presence of oxygen to produce a solid metal sulfate product and a gaseous product which is primarily SO<sub>3</sub>, wherein said metal is selected from the group consisting of iron, copper, zinc, nickel, cobalt and manganese. Said metal sulfate product is then leached with dilute sulfuric acid to form a metal-containing solution, from which the metal values are separated by precipitation at raised H<sub>2</sub>SO<sub>4</sub>-concentrations obtained by saturating the solution with the gaseous SO<sub>3</sub> from the sulfatization reaction step.

*Wolff, Bregman and Goller*

PATENT AND TRADE MARKS ATTORNEYS JC08 Rec'd PCT/PTO

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April 9, 2001

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VIA FACSIMILE  
49-89-239-94465  
AND VIA COURIER

Re: International Patent Appn. No. PCT/IL00/00513  
in the name of JOMA CHEMICAL AS  
Our Ref: 131,652 PCT

Dear Sirs:

Transmitted herewith please find one copy of an amended claim pages 9 and 10 to replace original pages 9 and 10 of the specification filed.

Following receipt of the International Search Report, the Applicant wishes to amend the claims under PCT Article 19 and we are accordingly filing with the confirmation copy of this letter being sent by courier, three copies of an amended sheets 9 and 10 to replace sheets 9 and 10 of the specification as filed.

Claims 1, 3, 4 and 6 have been replaced by amended claim 1, wherein claim 1, line 1 has been amended to clarify that the metal containing sulfide ores and concentrates are "treated" and line 2 has been amended to clarify that it is said metal containing sulfide ores and concentrates, i.e., the metal containing sulphidic materials which are reacted, claim 3 has been amended to indicate, as seen in the examples that the preferred embodiment is a stage-wise process and to clarify the precipitation of metallic sulphates from the solution, the dependency of claim 4 has been corrected and the language of claim 6 rendered more precise.

Very truly yours,

WOLFF, BREGMAN AND GOLLER

*G. Goller*  
Gilbert Goller, Patent Attorney  
Agent for Applicant

**WHAT IS CLAIMED IS:**

1. A hydrometallurgical process for producing metal-containing sulfide ores and concentrates, comprising reacting said metal-containing sulfide with concentrated sulfuric acid at a temperature of between about 300°C and 400°C in the presence of oxygen to produce a solid metal sulfate product and a gaseous product which is primarily SO<sub>3</sub>, wherein said metal is selected from the group consisting of iron, copper, zinc, nickel, cobalt and manganese.
2. A process according to claim 1, wherein said metal sulfate product is then leached with a dilute solution of sulfuric acid, having a concentration of between 5% and 35% to extract metal values therefrom and to form a metal-containing solution.
3. A process according to claim 2, wherein said SO<sub>3</sub> gaseous product formed from said reaction is subsequently combined with said metal-containing solution to raise the concentration of sulfuric acid in said solution to about 35% to 50% and to effect the precipitation of metal from said solution.
4. A process according to claim 4, wherein the amount of sulfuric acid upon mixing with one weight portion of sulfide ore is ≥0.94 weight portions of 98% sulfuric acid.
5. A process according to claim 1, wherein the sulfatization process is carried out at a temperature of between 330°C and 350°C.
6. A process according to claim 1, wherein the sulfatization process is carried out at constant oxidation with oxygen from air, its amount being ≥150% of the stoichiometrically required amount.
7. A process according to claim 1, wherein leaching of the sulfatized product is carried out in solution of sulfuric acid, having a concentration of about 15% to 25%.
8. A process according to claim 3, wherein separation of metal sulfate from the solution was made by its precipitation in sulfuric acid solutions of 40%-45% H<sub>2</sub>SO<sub>4</sub>.
9. A process according to claim 8, wherein a high concentration of sulfuric acid is achieved by saturation of the solution with gas SO<sub>3</sub> at room temperature.

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10. A process according to claim 9, wherein purification of sulfuric acid from the admixtures aimed at production of the acid ready for sale was performed by saturation with gas SO<sub>3</sub> up to a concentration of sulfuric acid of 98.3%.
11. A process according to claim 1, wherein said metal is iron.

**(19) World Intellectual Property Organization  
International Bureau**



A standard 1D barcode is located at the bottom of the page, spanning most of the width. It is used for document tracking and identification.

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(72) Inventor; and

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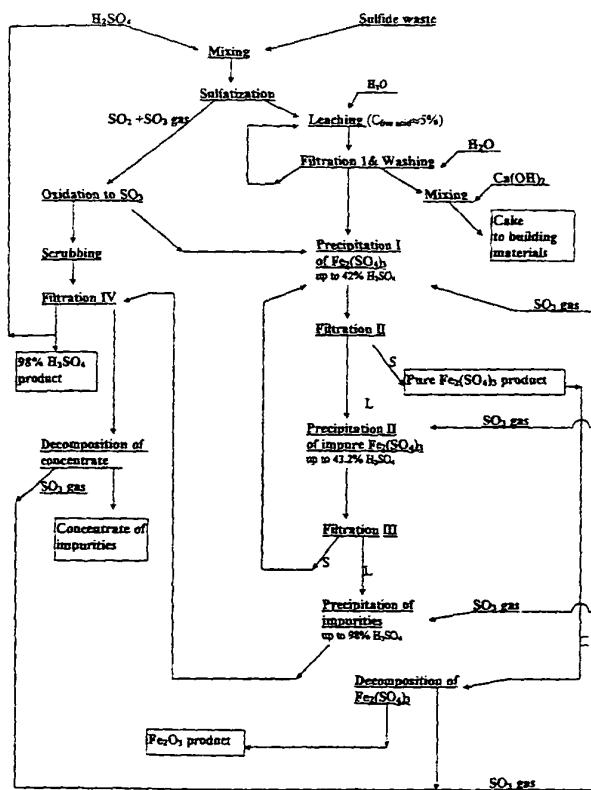
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[Continued on next page]

**(54) Title: SULFATISATION PROCESS FOR METAL EXTRACTION FROM SULFIDE ORES**



**(57) Abstract:** The invention provides a hydrometallurgical process for treating metal-containing sulfide ores and concentrates, comprising reacting said metal-containing sulfide with concentrated sulfuric acid at a temperature of between about 300 °C and 400 °C in the presence of oxygen to produce a solid metal sulfate product and a gaseous product which is primarily SO<sub>3</sub>, wherein said metal is selected from the group consisting of iron, copper, zinc, nickel, cobalt and manganese. Said metal sulfate product is then leached with dilute sulfuric acid to form a metal-containing solution, from which the metal values are separated by precipitation at raised H<sub>2</sub>SO<sub>4</sub>-concentrations obtained by saturating the solution with the gaseous SO<sub>3</sub> from the sulfatization reaction step.



patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

— *Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.*

**Published:**

— *With international search report.*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## SULFATISATION PROCESS FOR METAL EXTRACTION FROM SULFIDE ORES

**Technical Field**

The present invention relates to the field of hydrometallurgical processing of sulfide metal-containing ores and sulfide waste (dump sulfide tails) obtained after separation of sulfide concentrates of zinc, copper etc. by flotation aimed at production of metal sulfates, oxides, and other compounds as well as sulfuric acid, wherein said metal is selected from the group consisting of iron, copper, zinc, nickel, cobalt and manganese.

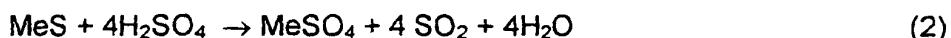
**Background Art**

The method for calcination of iron sulfides, pyrite, marcasite etc. at a high temperature  $\geq 900^{\circ}\text{C}$  according to the reaction:



is known. The escaping gas is converted to sulfuric acid, and a calcine ( $\text{Fe}_2\text{O}_3$ ) is used for production of various iron compounds or applied in ferrous metallurgy to obtain metal iron. However, because of a high residual content of sulfur in the calcine, its application in metallurgy is limited and it is usually dumped. [Short Chemical Encyclopedia, Moscow, 1979].

There is known a method of sulfatization of sulfide materials by their treatment with concentrated sulfuric acid at  $200^{\circ}\text{C} - 300^{\circ}\text{C}$  [Pat US 1895811, 1933; L.E.Makovezky, H.Morgan]. This process is described by a reaction:



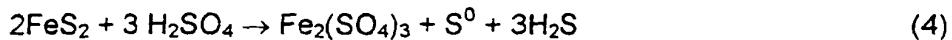
where Me - Fe, Ni, Zn, Cu etc.

However, the largest extent of sulfatization (78.4%) of pyrite ( $\text{FeS}_2$ ) was achieved at  $200^{\circ}\text{C}$ , the sulfatization extent of copper sulfides was lower.

With temperature increase to  $300^{\circ}\text{C}$  the reaction of pyrite sulfatization proceeds as follows:



At a temperature  $300^{\circ}\text{C}$  sulfuric acid behaves as a strong oxidizer and a portion of iron is oxidized to Fe(III) [S.S.Naboichenko, V.I.Smirnov "Hydrometallurgy of copper", Moscow, "Metallurgiay", 1974]:



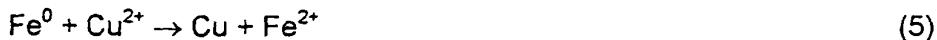
There exists a method for sulfatization of zinc and copper sulfides by their dissolving in sulfuric acid of a high concentration (45 - 70%) at a temperature below the boiling point of these solutions (for 45%  $H_2SO_4$  -  $\leq 130^\circ C$ ; for 70%  $H_2SO_4$  -  $\leq 140^\circ C$ ). Under these conditions zinc sulfate was obtained ( $ZnSO_4 \cdot H_2O$ ), sulfatization of copper and iron sulfates proceeded incompletely [Pat. US 5711922, Jan.27.1998; O'Brien, Robert N.].

Sulfide ores and concentrates can be also treated with a mixture of sulfuric and nitric acids at 110 - 170°C. Sulfuric acid concentration is 40 - 65%. The amount of nitric acid required for sulfatization is 0.5 - 3.0 moles of  $HNO_3$  per 1 mole of sulfides which are contained in the treated material [Pat. US 5484579, Jan.16, 1996; O'Brien, Robert N.]. This technology does not provide a complete sulfatization of metal sulfides as well. In addition a complicated problem of utilization of gases  $SO_2$  and  $SO_3$ , which contain nitrogen oxides arises.

All the patents mentioned above deal with a complicated and yet unsolved problem of separation of admixtures of sulfates of such metals as Al, Cu, Zn, Ni etc. from iron sulfates.

Usually the solution of metal sulfates obtained after sulfatization and leaching is oxidized with oxygen of air or by other methods in order to convert  $Fe^{2+}$  to  $Fe^{3+}$ , then the solution is adjusted to pH=2, iron precipitates as  $Fe(OH)_3$ , and the admixtures remain in solution. To obtain iron (III) sulfate, iron hydroxide is again dissolved in sulfuric acid. Extraction of admixtures from the sulfuric acid solution is a complicated problem.

If the solution obtained after sulfatization contains a large amount of copper, the method of cementation with iron scrap is applied. It is described by the following reactions:



Copper precipitates as a metal powder, and iron converts to its bivalent form  $FeSO_4$ , all admixtures, except for copper, are in solution with iron. Isolation of pure iron sulfate from this solution is a large technological problem.

The present invention is aimed at the development of the method for processing sulfide ores and concentrates, in particular pyrite, performed at lower temperatures than pyrite calcination and which results in the production of highly

pure iron sulfates without using additional amounts of reagents for neutralization of strongly acidic solutions.

**Disclosure of the Invention.**

Thus, according to the present invention, there is now provided a hydrometallurgical process for producing metal-containing sulfide ores and concentrates, comprising reacting said metal-containing sulfide with concentrated sulfuric acid at a temperature of between about 300°C and 400°C in the presence of oxygen to produce a solid metal sulfate product and a gaseous product which is primarily SO<sub>3</sub>, wherein said metal is selected from the group consisting of iron, copper, zinc, nickel, cobalt and manganese.

In preferred embodiments of the present invention said metal is iron.

In preferred embodiments of the present invention said metal sulfate product is then leached with a dilute solution of sulfuric acid, having a concentration of between 5% and 35% to extract iron values therefrom and to form an iron-containing solution.

In especially preferred embodiments of the present invention said SO<sub>3</sub> gaseous product formed from said reaction is subsequently combined with said metal-containing solution to raise the concentration of sulfuric acid in said solution to about 35% to 50% and to effect the precipitation of said metal from said solution.

Thus, in a most preferred embodiment of the present invention the milled sulfide ore, particularly pyrite FeS<sub>2</sub>, is mixed with concentrated (98.3%) sulfuric acid and calcined in a furnace at a temperature about 338.8°C and at a constant blowing of air or air enriched with oxygen.

A temperature 338.8°C is the maximum temperature for sulfuric acid solutions, this is the boiling temperature of azeotrope containing 98.3% of H<sub>2</sub>SO<sub>4</sub>. With a temperature rise pyrite and other sulfides much better interact with sulfuric acid. In addition, an application of oxygen of air results in the following reaction for this process:



The product resulted from sulfatization was leached in diluted solution of sulfuric acid ( $\leq 36\%$  at  $\approx 90 - 100^\circ\text{C}$ ). The extraction of iron to solution was 95%, of them 92.15% was in a form of Fe(III).

After leaching the unsolved cake, containing  $\text{SiO}_2$ ,  $\text{CaSO}_4$ , aluminosilicates etc, was separated from the solution by filtration. Then gas  $\text{SO}_3$ , formed in the sulfatization process, was blown through the solution so that to increase the concentration of sulfuric acid to 42% (Precipitation I)



At such a concentration of sulfuric acid 89.1% of iron was salted out (precipitated) as highly pure  $\text{Fe}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{SO}_4$ . This product was filtered off, and gas  $\text{SO}_3$  was continuously blown through the solution to a concentration of sulfuric acid 43.0 - 43.2%  $\text{H}_2\text{SO}_4$ . During this process rather unpure crystals of  $\text{Fe}_2(\text{SO}_4)_3$  precipitated (Precipitation II), which were returned to stage Precipitation I for further purification. Solutions after Precipitation II were saturated with  $\text{SO}_3$  to  $\text{H}_2\text{SO}_4$  concentration 98.3%. At such a concentration of sulfuric acid practically all the admixtures precipitated (Precipitation III), filtered off and used for production of a concentrate of nonferrous metals. The sulfuric acid composition corresponded to that of sulfuric acid produced for sale. The acid was partially returned to the head of the process for sulfatization, partially it was used as a product ready for sale.

Iron sulfate crystals obtained after Precipitation I were decomposed at  $\approx 700^\circ\text{C}$



Gas  $\text{SO}_3$  formed in this process is used at one of the precipitation stages. The admixtures after precipitation III are sulfates of such metals as Al, Ti, Zn and others. After filtration they were decomposed at  $600^\circ\text{C}$  -  $700^\circ\text{C}$ :



The escaping gas  $\text{SO}_3$  was also used for precipitation, and the residual formed after calcination is a concentrate of nonferrous metal oxides. The composition of this concentrate depends on the composition of a raw material used.

The invention will now be described in connection with certain preferred embodiments with reference to the attached flow sheet and the following examples so that it may be more fully understood.

With specific reference now to the examples, it is stressed that the particulars discussed are by way of example and for purposes of illustrative discussion of the preferred embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood

description of the principles and conceptual aspects of the invention. It is not intended, however, to limit the invention to these particular embodiments. On the contrary, it is intended to cover all alternatives, modifications and equivalents as may be included within the scope of the invention as defined by the appended claims. Thus, the following examples which include preferred embodiments will serve to illustrate the practice of this invention, it being understood that the particulars shown are by way of example and for purposes of illustrative discussion of preferred embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of formulation procedures as well as of the principles and conceptual aspects of the invention.

### **Description of Preferred Embodiments**

#### **Example 1.**

Sulfide waste, which was obtained from sulfide ore after separation of zinc and copper concentrates by flotation, is used as a raw material. Sulfide waste has the following composition: Fe - 34.0%; Al - 3.34%; Ca 3.37%; Mg - 3.08%; Ti - 0.72%; Zn - 0.21%; Pb - 0.03%; Cu - 0.15%; Mn - 0.07%; Ni - 0.003%; Co - 0.015%; V - 0.02%; Na - 0.023%; K - 0.14%; As - 0.04%; Ag - 3.2  $10^{-4}\%$ ; S - 22.6%; Si - 4.97%; H<sub>2</sub>O - 9.1%, and the following fraction analysis:

Particle size, micron	Fraction content, %
+350	0.90
+210	4.82
+99	16.07
+75	14.63
+44	34.13
-44	29.45
In total	
	100%

A sample of sulfide waste was milled in a ball mill to a size -75 micron -100%, then it was mixed at room temperature with concentrated sulfuric acid in a ratio 1:0.94 by weight. Mixing was made during 30 min., then the mixture obtained was loaded to a tube furnace, where the sulfatization process occurred at 338°C. Air was blown during the sulfatization process. The amount of air required was 1900 l/1 kg of sulfide waste, that is 200% of the amount theoretically required according to

reaction (7). Sulfatization time is 2 hours. Gas SO<sub>3</sub> escaping at sulfatization is forwarded to scrubbers for precipitations I, II or III. The product resulted from sulfatization was loaded to a reactor for leaching (2.4 litters of 20% H<sub>2</sub>SO<sub>4</sub> per 1 kg of the sulfatized product). Leaching was performed at a temperature 90 - 100°C for 2 hours at constant stirring, the pulp was filtered on a vacuum filter, the solution goes in a scrubber for precipitation of pure iron (III) sulfate (Precipitation I), and the cake is washed with water on a filter. Sulfuric acid was added to wash water to a concentration ≈20% and used for leaching of the following portion of the sulfatization product.

The cake after washing contained 0.1% H<sub>2</sub>SO<sub>4</sub> free; 11.5% CaSO<sub>4</sub>; 10.65% SiO<sub>2</sub>; Al<sub>2</sub>O<sub>3</sub>; TiO<sub>2</sub> and other admixtures. It was neutralized by slaked lime [Ca(OH)<sub>2</sub>] that resulted in an increase in CaSO<sub>4</sub> content to 33-34%. This product can be used as a building material.

After leaching the solution contained 95.8g/l Fe (342.8 g/l Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>), it was used for Precipitation I. The crystals obtained after Precipitation II were returned to this solution.

Precipitation I was made at room temperature by blowing SO<sub>3</sub> (gas) in order to increase the sulfuric acid concentration in solution to 42%. At such a concentration of sulfuric acid ≥89.1% Fe precipitated in a form of chemically pure complex salt Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> ·4H<sub>2</sub>SO<sub>4</sub>; ≥99.7% of admixtures remained in solution.

Iron sulfate Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> ·4H<sub>2</sub>SO<sub>4</sub> was filtered on a vacuum filter, filtrate was used in the Precipitation II stage, and the salt was decomposed at a temperature 600-700°C for 1 hour. The formed gas SO<sub>3</sub> and sulfuric acid vapor were applied to precipitate iron salts, admixtures, and to produce sulfuric acid for sale in accordance with the given technological scheme. The product obtained after calcination contained ≥99.7% of Fe<sub>2</sub>O<sub>3</sub>, by its physical and chemical properties it was iron-oxide pigment of high quality. This product can be used both for the production of the high quality iron powder and various iron compounds (Fe<sub>3</sub>O<sub>4</sub> etc.). The filtrate after Precipitation I contained 42% H<sub>2</sub>SO<sub>4</sub>; 21.6 g/l Fe. At stage Precipitation II it was saturated with SO<sub>3</sub> gas to a concentration of sulfuric acid in solution equal to 43.2%, the iron content in solution decreased to 7.7g/l. A portion of admixtures, about 2% of the total amount in the raw material, was precipitated together with iron (III) sulfate

crystals. The crystals were filtered and then used in Precipitation I, and the solution containing admixtures was forwarded to precipitation III.

Precipitation III was also performed with  $\text{SO}_3$ 3recipitation III was also performed with  $\text{SOO}$ olution equal to 43.2%, the iron content in solution decreased to 7.7g/l. A portion of admixtures, about 2% of the total amount in the raw material, was precipitated together with iron (III) sulfate crystals.  $\text{SO}_3$ 3recipitation III was also performed with  $\text{SOO}$ olution equal to 43.2%, the iron content in solution decreased to 7.7g/l. A portion of admixtures, about 2% of the total amount in the raw material, was precipitated together with iron (III) sulfate crystals.  $\text{SO}_3$ 3recipitation III was also performed with  $\text{SOO}$ olution equal to 43.2%, the iron content in solution decreased to 7.7g/l. A portion of admixtures, about 2% of the total amount

#### **Comparative Example 2.**

Under conditions of example 1, one weight portion of sulfide waste was mixed with 0.72 weight portions of 98.3%  $\text{H}_2\text{SO}_4$ , that was 80% of the theoretically required amount of sulfuric acid. After sulfatization about 70% of iron yielded to solution.

#### **Example 3.**

Under conditions of example 1, one weight portion of sulfide waste was mixed with 1.1 weight portions of 98.3%  $\text{H}_2\text{SO}_4$  (120% of the theoretically required amount). The iron yield to solution was 95%.

#### **Comparative Example 4.**

Under conditions of example 1, sulfatization was performed at a temperature 250°C. The yield of iron in solution was 66%.

#### **Example 5.**

Under conditions of example 1, sulfatization was performed at a temperature 350°C. The yield of iron in solution was 95%.

#### **Example 6.**

Under conditions of example 1, the sulfatization was performed at the air amount equal to 100% of the stoichiometric amount. Elementary sulfur and  $\text{SO}_2$  were formed, about 30% of iron was in its bivalent form.

#### **Comparativ Example 7.**

Under conditions of example 1, leaching of the sulfatization product was made in 2% sulfuric acid solution (20g/l H<sub>2</sub>SO<sub>4</sub>). The yield of iron to solution was 70%.

**Example 8.**

Under conditions of example 1 leaching was made in solution of 5% sulfuric acid. The yield of iron to solution was 94.5%.

**Example 9.**

Under conditions of example 1, leaching was made in 35% sulfuric acid solution. The yield of iron to solution was 94.8% because of the partial precipitation of iron sulfate.

**Comparative Example 10.**

Under conditions of example 1, precipitation of iron sulfate was performed by saturation of the solution with SO<sub>3</sub> gas up to H<sub>2</sub>SO<sub>4</sub> concentration equal to 40%. Iron yield in pure crystals was 75%.

**Example 11.**

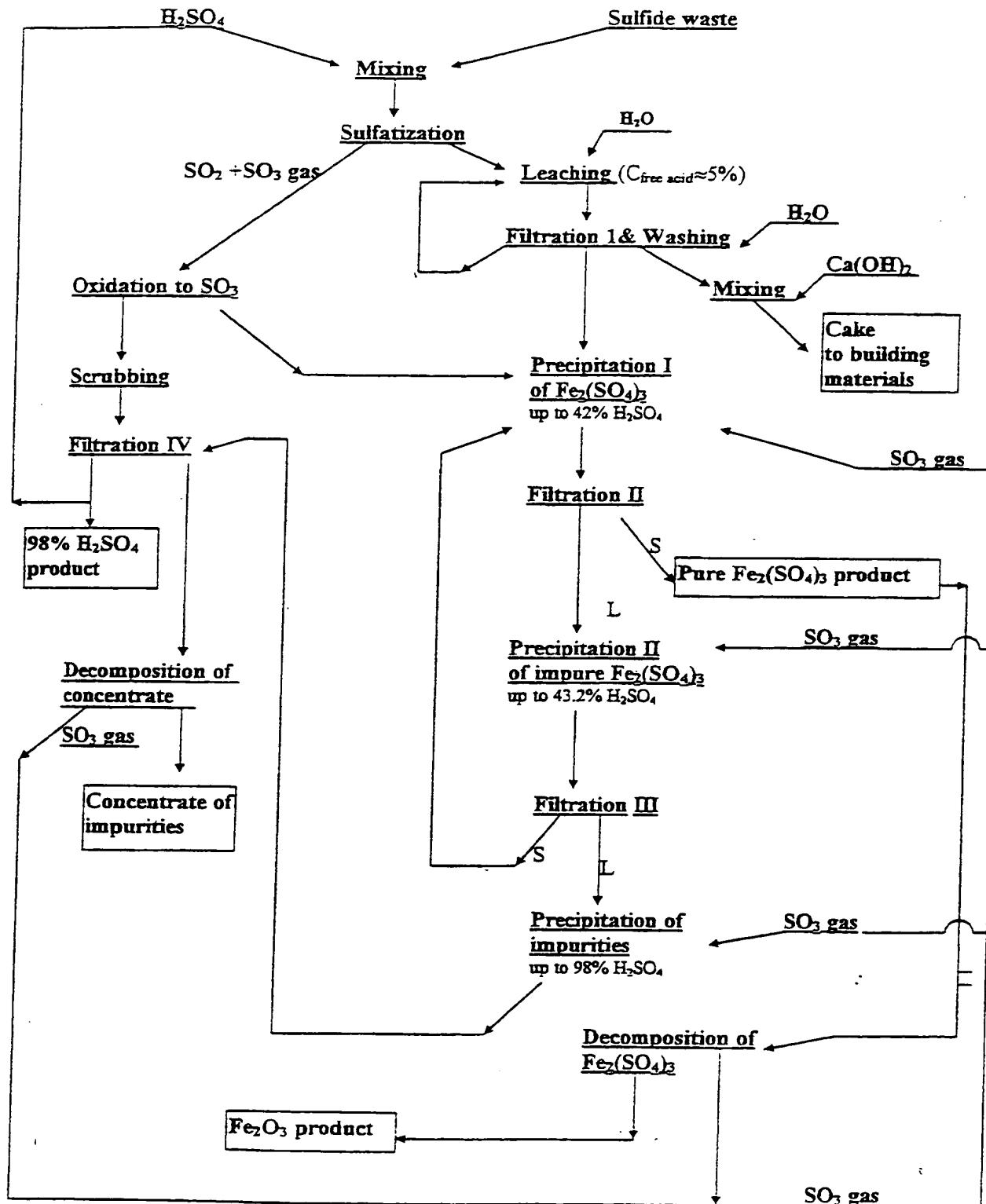
Under conditions of example 1 precipitation of iron sulfate was made by saturation of the solution with gas SO<sub>3</sub> up to a sulfuric acid concentration 45%. Iron yield in crystals increased to 93%, however, Fe<sub>2</sub>O<sub>3</sub> obtained from these crystals and contained 98% of Fe<sub>2</sub>O<sub>3</sub> and 2% of oxides of other metals.

It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative examples and that the present invention may be embodied in other specific forms without departing from the essential attributes thereof, and it is therefore desired that the present embodiments and examples be considered in all respects as illustrative and not restrictive, reference being made to the appended claims, rather than to the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

**WHAT IS CLAIMED IS:**

1. A hydrometallurgical process for producing metal-containing sulfide ores and concentrates, comprising reacting said metal-containing sulfide with concentrated sulfuric acid at a temperature of between about 300°C and 400°C in the presence of oxygen to produce a solid metal sulfate product and a gaseous product which is primarily SO<sub>3</sub>, wherein said metal is selected from the group consisting of iron, copper, zinc, nickel, cobalt and manganese.
2. A process according to claim 1, wherein said metal sulfate product is then leached with a dilute solution of sulfuric acid, having a concentration of between 5% and 35% to extract metal values therefrom and to form a metal-containing solution.
3. A process according to claim 2, wherein said SO<sub>3</sub> gaseous product formed from said reaction is subsequently combined with said metal-containing solution to raise the concentration of sulfuric acid in said solution to about 35% to 50% and to effect the precipitation of metal from said solution.
4. A process according to claim 4, wherein the amount of sulfuric acid upon mixing with one weight portion of sulfide ore is  $\geq 0.94$  weight portions of 98% sulfuric acid.
5. A process according to claim 1, wherein the sulfatization process is carried out at a temperature of between 330°C and 350°C.
6. A process according to claim 1, wherein the sulfatization process is carried out at constant oxidation with oxygen from air, its amount being  $\geq 150\%$  of the stoichiometrically required amount.
7. A process according to claim 1, wherein leaching of the sulfatized product is carried out in solution of sulfuric acid, having a concentration of about 15% to 25%.
8. A process according to claim 3, wherein separation of metal sulfate from the solution was made by its precipitation in sulfuric acid solutions of 40%-45% H<sub>2</sub>SO<sub>4</sub>.
9. A process according to claim 8, wherein a high concentration of sulfuric acid is achieved by saturation of the solution with gas SO<sub>3</sub> at room temperature.

10. A process according to claim 9, wherein purification of sulfuric acid from the admixtures aimed at production of the acid ready for sale was performed by saturation with gas  $\text{SO}_3$  up to a concentration of sulfuric acid of 98.3%.
11. A process according to claim 1, wherein said metal is iron.



# INTERNATIONAL SEARCH REPORT

Int: International Application No

PCT/IL 00/00513

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 C22B1/06 C22B19/02 C22B15/00 C22B19/20 C22B3/08  
C22B23/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 003 740 A (HUGGINS DALE K ET AL) 18 January 1977 (1977-01-18) column 3, line 27 - line 40	1,2,5
Y	column 3, line 53 - line 63 ---	7
Y	FR 2 463 189 A (METALLURGIE HOBOKEN) 20 February 1981 (1981-02-20) page 1, line 13 - line 28; examples 1,3 ---	1,2,5,7
Y	US 4 119 698 A (ZIMMER ERICH ET AL) 10 October 1978 (1978-10-10) column 2, line 29 - line 45 ---	1,2,5,7
Y	AU 35116 71 A (THE AUSTRALIAN MINERAL DEVELOPMENT LABORATORIES) 3 May 1973 (1973-05-03) page 2 -page 3 ---	1,2,5,7
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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- °X° document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- °Y° document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- °&° document member of the same patent family

Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

Int. Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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